

This Page Is Inserted by IFW Operations  
and is not a part of the Official Record

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning documents *will not* correct images,  
please do not report the images to the  
Image Problem Mailbox.**

12

# EUROPEAN PATENT APPLICATION

21 Application number: 85113834.7

51 Int. Cl.<sup>4</sup>: H 01 M 8/04

22 Date of filing: 30.10.85

30 Priority: 31.10.84 JP 229277/84  
10.04.85 JP 74264/85

43 Date of publication of application:  
21.05.86 Bulletin 86/21

84 Designated Contracting States:  
DE FR GB

71 Applicant: HITACHI, LTD.  
6, Kanda Surugadai 4-chome Chiyoda-ku  
Tokyo 100(JP)

72 Inventor: Tsukui, Tsutomu  
15-6, Ishinazakacho-1-chome  
Hitachi-shi(JP)

72 Inventor: Yasukawa, Saburo  
20-13, Higashioshima-1-chome  
Katsuta-shi(JP)

72 Inventor: Shimizu, Toshio  
3473-3, Higashiishikawa  
Katsuta-shi(JP)

72 Inventor: Doi, Ryota  
308-2, Minamigo Nukada Nakamachi  
Naka-gun Ibaraki-ken(JP)

72 Inventor: Yamaguchi, Motoo  
2-8, Kanesawacho-7-chome  
Hitachi-shi(JP)

72 Inventor: Iwaasa, Shuzou  
10-12, Suehirocho-3-chome  
Hitachi-shi(JP)

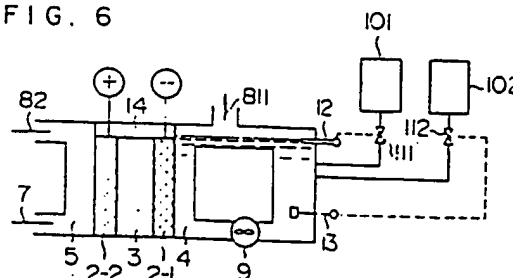
74 Representative: Patentanwälte Beetz sen. - Beetz jun.  
Timpe - Siegfried - Schmitt-Fumian  
Steinsdorfstrasse 10  
D-8000 München 22(DE)

54 Liquid fuel cell.

57 A liquid fuel cell having a circulation system for a fuel mixture comprising fuel and water, which comprises a first tank (101) containing water or a water-rich fuel mixture comprising water and fuel, a second tank (102) containing fuel or a fuel-rich mixture comprising water and fuel, a first detector (12) for detecting the liquid level of the fuel mixture in the circulation system, a second detector (13) for detecting a fuel concentration of the fuel mixture in the circulation system, or an output from the fuel cell, or a load current of the fuel cell, a valve means (111) for controlling flow of the water or the water-rich mixture in the first tank to the circulation system in accordance with the output from the first detector (12), and a valve means (112) for controlling flow of the fuel or the fuel-rich mixture in the second tank (102) to the circulation system in accordance with the output from the second detector (13). The liquid fuel cell can be stably and efficiently operated for a prolonged time in spite of different consumption rates of fuel and water even if the load current or operating temperature of the fuel cell or the

temperature or humidity of the atmosphere is changed.

FIG. 6



## LIQUID FUEL CELL

## 1 BACKGROUND OF THE INVENTION

This invention relates to a liquid fuel cell, and particularly to a liquid fuel cell capable of stable operation for a prolonged time under controlled supply of  
5 fuel and water.

Generally, fuel cells using a liquid fuel are classified into an acid type and an alkali type, and methanol, formalin, hydrazine, etc. are used as fuel. The working principle of such fuel cells will be briefly  
10 described, referring to Fig. 1, where numeral 1 shows a fuel cell and symbols + and - show terminals for outputting electricity. The fuel cell 1 comprises a fuel electrode 2-1, an oxidizing agent electrode 2-2 counterposed to the fuel electrode 2-1 (the oxidizing agent electrode can be  
15 called "oxygen electrode" when oxygen is used as an oxidizing agent, or "air electrode" when air is used as an oxidizing agent), an electrolyte chamber provided between the oxidizing agent electrode 2-2 and the fuel electrode 2-1, a fuel chamber 4 provided adjacent to the fuel  
20 electrode 2-1, and an oxidizing agent chamber 5 provided adjacent to the oxidizing agent electrode 2-2. In Fig. 1, numeral 6 shows the fuel (which may contain water), or a mixture of fuel and electrolyte and also shows its flow direction, and numeral 7 likewise shows the oxidizing agent  
25 and also shows its flow direction.

1           The fuel cell as structured above works as  
follows. When the fuel 6 is supplied to the fuel chamber  
4 and when the oxidizing agent 7 is supplied to the  
oxidizing chamber 5, the fuel 6 permeates into the fuel  
5 electrode 2-1 to generate electrons through the electro-  
chemical reaction. When a load is given to the external  
circuit, a direct current can be obtained. In this case,  
a product 81 is formed in the fuel chamber 4. The product  
is a carbon dioxide gas or carbonate when the fuel is  
10 methanol, formic acid or formalin, and nitrogen when the fuel  
is hydrazine. When the supply of fuel 6 of a circulating  
type, the product contains excess fuel or electrolyte, and  
it is necessary to separate and vent the gaseous product  
from the circulation system.

15           On the other hand, when the oxidizing agent 7 is  
supplied to the oxidizing agent chamber 5, the oxidizing  
agent 7 permeates and diffuses into the oxidizing agent  
electrode 2-2 to consume electrons through the electro-  
chemical reaction. When the electrolyte is of an acid type,  
20 a product 82 is formed. The product is mainly water and  
contains excess air. When the electrolyte is of a base type,  
water is formed at the fuel electrode 2-1.

          When an aqueous solution of electrolyte such as  
sulfuric acid or potassium hydroxide is used in the  
25 electrolyte chamber 3 in the unit fuel cell 1 structured as  
in Fig. 1, the aqueous solution leaks from the electrolyte  
chamber 3 and thoroughly permeates also into the electrodes,  
and a good cell performance can be obtained. However, the

1 aqueous solution of electrolyte also leaks into the fuel  
chamber 4 in this case, and thus it is necessary to supply  
fuel mixture containing the aqueous solution of electrolyte  
prepared in advance as anolyte. To this end, the fuel  
5 chamber 4 is provided with a circulation system for supply-  
ing the fuel mixture to the fuel chamber 4 by a pump 9 and  
a system for supplying the fuel from a fuel tank 10 through  
a valve 11 to the circulation system, as shown in Fig. 2.

It has been also proposed to use an aqueous  
10 solution of polymeric electrolyte in the electrolyte  
chamber 3 in place of the acid electrolyte, and provide the  
fuel chamber with a circulation system for a fuel mixture  
of fuel and water adjusted to a most suitable concentra-  
tion for the operation as in Fig. 2, and also with a system  
15 for supplying the fuel from the fuel tank 10 to the  
circulation system.

As shown in Fig. 2, the product gas 811 is vented  
from the circulation system after the passage through the  
fuel chamber 4, and the remaining mixture 812 is recycled  
20 to the fuel chamber.

According to the conventional fuel supply system  
as described above, a fuel mixture in a constant mixing  
ratio prepared in advance is supplied to the circulating  
system from the single fuel tank 10 shown in Fig. 2.  
25 However, it has been found that the consumption ratios of  
fuel and water in the circulation mixture 6 containing the  
fuel are not always constant, and depend on changes in load,  
changes in temperature of fuel cell during the operation,

1 even though the load is constant, or changes in flow rate and  
temperature or humidity of the air supplied as the oxidizing  
agent.

In a fuel cell using a liquid fuel, the fuel  
5 supply system contains two essential components, i.e. fuel  
and water, and further may contain an electrolyte. In the  
most cases, these three components, i.e. fuel, water and  
electrolyte are usually contained in the fuel supply system.  
Among these three components, it is the fuel and water that  
10 are consumed. Usually, it is not necessary to take  
consumption of electrolyte into consideration. Consumption  
rate of fuel differs from that of water, because firstly  
water is always consumed at one electrode, whereas at  
another electrode water is always formed as a result of the  
15 electromotive reaction of a fuel cell, and formation of  
water at the fuel electrode or the oxidizing agent electrode,  
depends on the acidity or the alkalinity of electrolyte.  
That is, in the case of an acidic electrolyte, water is  
formed at the oxidizing agent electrode and consumed at the  
20 fuel electrode, whereas in the case of an alkaline  
electrolyte, the formation and consumption of water are  
reversed. In that case, one mole or two moles of water is  
principally formed with one mole of fuel throughout the  
reaction, depending on the species of fuel. Since the  
25 consumption and formation of water take place at the  
different electrodes, water actually tends to migrate  
through the electrolyte chamber to keep a water balance.  
Even in view of this tendency, water is short at one

1 electrode and in excess at another electrode, owing to much  
dissipation of water and difficulty to keep the water  
balance well throughout the electrolyte chamber.

Secondly, the excess or shortage of water due to  
5 water imbalance in the water migration between the  
electrodes largely depends on the operating temperature and  
the load current.

Thirdly, the excess fuel that is not converted to  
the electric current at the fuel electrode migrates through  
10 the electrolyte chamber and permeates into the oxidizing  
agent electrode to occasion direct oxidation of the fuel,  
or water migrates as hydronium ions when the electrolyte  
ions migrate in the electrolyte chamber in the case of an  
acidic electrolyte. These phenomena also depend on the  
15 load current and operating temperature of a fuel cell.  
Furthermore, the amount of water carried by the oxidizing  
agent, for example, air by evaporation at the oxidizing  
agent electrode side depends on the feed rate, temperature  
and humidity of the oxidizing agent.

20 The consumption rate of fuel differs from that  
of water on the grounds as described above, and thus the  
supply of a mixture of fuel and water only in a constant  
mixing ratio from a single tank to the fuel circulation  
system as shown in Fig. 2 can only meet a change in the  
25 amount of only one component among the two components, i.e.  
fuel and water, in the fuel circulation system including  
the fuel chamber. That is, adequate control over the fuel  
and water cannot be made, and stable and prolonged operation

In a fuel cell using a liquid fuel, the cell voltage  $V$  shows a flat peak in a certain range of concentration  $C_m$  of fuel 6 when the current is constant. At a lower fuel concentration  $C_m$ , the fuel becomes short and the cell voltage is lowered, whereas at a higher fuel concentration  $C_m$ , the excess fuel that fails to take part in the reaction at the fuel electrode 2-1 migrates through the electrolyte chamber 3 and permeates into the oxidizing agent electrode 2-2 to occasion direct combustion of fuel. As a result, the potential on the oxidizing agent electrode 2-2 is lowered with generation of heat, and consequently the cell voltage is lowered. When the fuel concentration is too high or too low (e.g. less than  $C_{m1}$  or more than  $C_{m2}$  in Fig. 3), the ratio of the necessary amount of electrical energy-converted fuel to the amount of consumed fuel will be lowered, and thus the fuel utilization efficiency is considerably lowered. Thus, it is very important to select an appropriate fuel concentration.

SECRETARY OF THE ARMY



1 electrolyte type fuel cell using methanol as fuel, it is  
disclosed in 24th Cell Panel Discussion Lectures No. 2B02,  
page 254 that the concentration  $C_{m1}$  is 0.5 moles/l and the  
concentration  $C_{m2}$  is 2 moles/l at the current density of  
5 mA/cm<sup>2</sup>. Japanese Patent Application Kokai (Laid-open)  
No. 56-118273 discloses that the concentration  $C_{m2}$  is  
about 5% by weight (about 1.6 moles/l).

On the other hand, even in a liquid fuel cell  
using hydrazine as fuel, Japanese Patent Publication No.  
10 48-31300 discloses that stable operation is possible at  
1.5% by weight (0.5 moles/l), and if the concentration is  
less than 1.5% by weight, the voltage is lowered and the  
temperature is increased.

It is seen from the foregoing that the fuel  
15 concentration range for stable operation is about 0.3  
moles/l as  $C_{m1}$  and about 2 moles/l as  $C_{m2}$ .

Thus, the fuel concentration is very important  
in the fuel cell, and a more accurate apparatus for detecting  
or measuring the fuel concentration is still required.

20 A liquid fuel cell provided with an apparatus for  
detecting a fuel concentration now in practical use is  
shown in Fig. 4, where the same members as in Fig. 1 and  
Fig. 2 are indicated with the same reference numerals.

An oxidizing agent 7 is supplied to an oxidizing  
25 agent chamber 5 by a blower 111, and discharged as a  
residual gas 82. On the other hand, a fuel supply system  
includes a system for circulating a mixture of fuel and an  
electrolyte solution (the mixture may be called "anolyte")

1 by a pump 9 and a system for supplying an appropriate  
amount of fuel to an anolyte tank 20 provided in the  
circulation system from a fuel tank 10 through a valve 17.  
The circulation system is open to the outside at an  
5 appropriate position to discharge the product gas 811.

The fuel is supplied by opening the valve 17, and  
the opening or closure or control of the valve 17 is made  
by an apparatus 13 for detecting a fuel concentration  
provided in the anolyte tank 20 and a valve controller 171.

10 The apparatus 13 for detecting a fuel concentra-  
tion comprises an anode electrode 517 (which will be herein-  
after referred to merely as "anode"), a cathode electrode  
518 counterposed to the anode (the cathode electrode will  
be hereinafter referred to merely as "cathode"), a power  
15 source 519, and a detector 520. The anode 517 comprises a  
platinum plate 517a and a membrane 517b tightly laid on the  
platinum plate 517a by pressing.

With such a structure as described above, when a  
DC voltage of e.g. 0.85 V is applied to between the anode  
20 517 and the cathode 518, the quantity of electric current  
changes proportionally to the methanol concentration in the  
anolyte. Thus, it is possible to determine the concentra-  
tion of methanol as fuel in a very simple structure.

However, the concentration of methanol can be  
25 indeed determined by the apparatus with such a structure  
as described above, but its detection sensitivity is not  
better, as given below.

Relationship between the fuel concentration and

- 1 detected electric current is shown in Fig. 12, where curve  
a shows those determined by an apparatus for detecting a  
fuel concentration using an anode with the membrane as  
shown in Fig. 5. The electric current changes with  
5 concentration  $C_m$  but the change in electric current is  
small. That is, the detection sensitivity is poor.

- Furthermore, the adhesion between the platinum  
plate 517a and the membrane 517b (Fig. 5) is often  
inadequate, and the anolyte tends to stay therebetween,  
10 deteriorating the response to changes in the methanol  
concentration. When a platinum-based catalyst layer is laid  
on the platinum plate 517a in place of the membrane 517b,  
much detected current can be obtained as shown by curve b  
in Fig. 12, but there is no change in the detected current  
15 in the practical range (about 0.3 - about 2 moles/l) and  
such a structure cannot be used as a sensor.

- Cyclic voltammetry using a reference electrode  
and an apparatus for detecting a fuel concentration by means  
of a small fuel cell as disclosed in Japanese Patent  
20 Application Kokai (Laid-open) No. 56-118273 are also  
available as another apparatus for detecting a fuel concent-  
ration. In the case of the cyclic voltammetry, a reference  
electrode is required in addition to the detecting  
electrodes, and also a function generator and other devices  
25 are required, complicating the detecting system and  
deteriorating the reliability, the most important task of  
the sensor.

In the case of the apparatus using a small fuel

1 cell, not only the apparatus is dipped in the anolyte tank,  
but also an additional air supply system is required, and  
there is a difficulty in reduction in the apparatus size  
as well as in the reliability.

5 In the case of using methanol or formalin as  
fuel rather than using hydrazine as fuel, the detected power  
output changes in a complicated manner even according to  
the cyclic voltammetry, and the determination is sometimes  
difficult to make.

10 There is other procedure for supplying a fuel  
when an integrated load current becomes constant, since the  
fuel concentration is proportional to the load current, but  
when the load is greatly changed or the operation of fuel  
cell is subject to repetitions of discontinuation, the fuel  
15 concentration will be greatly deviated and cannot be  
practically determined. A gas concentration sensor based  
on semi-conductors requires much time until it is settled  
for the measurement, and thus the response becomes poor.

Thus, a liquid fuel cell with a reliable  
20 apparatus for detecting a fuel concentration in a simple  
structure is in keen demand.

#### SUMMARY OF THE INVENTION

An object of the present invention is to provide  
a liquid fuel with an improved supply of fuel and water to  
25 a fuel circulation system which can operate continuously  
and stably for a prolonged time in spite of differences in  
the consumption rates of fuel and water.

1           Another object of the present invention is to provide a liquid fuel cell with an apparatus for detecting a fuel concentration with a high reliability and a high sensitivity in a simple structure.

5           The present invention provides a liquid fuel cell having a circulation system for a fuel mixture comprising fuel and water, which comprises a first tank containing water or a water-rich fuel mixture comprising water and fuel, a second tank containing fuel or a fuel-rich  
10 mixture comprising water and fuel, a first detector for detecting the liquid level of the fuel mixture in the circulation system, a second detector for detecting a fuel concentration of the fuel mixture in the circulation system, or an output from the fuel cell, or a load current of the  
15 fuel cell, a valve means for controlling flow of the water or the water-rich mixture in the first tank to the circulation system in accordance with the output from the first detector, and a valve means for controlling flow of the fuel or the fuel-rich mixture in the second tank to the  
20 circulation system in accordance with the output from the second detector.

          According to the present invention, an apparatus for detecting a fuel concentration by electrochemical reaction, comprising an anode electrode provided with a  
25 fuel-controlling layer for controlling permeation of fuel through a catalyst layer, a cathode electrode, a power source and a detector, the anode electrode and the cathode electrode being dipped in the fuel mixture and a voltage

1 being applied to the electrodes is used as a second  
detector in the present liquid fuel cell.

Fuel cannot be too concentrated in the fuel circulation system, because at a higher fuel concentration, excess fuel is liable to permeate into the oxidizing agent electrode from the fuel electrode through the electrolyte chamber, and undergo direct oxidation, i.e. direct consumption, considerably lowering the fuel utilization efficiency. Usually the fuel concentration in the fuel circulation system is about 0.3 to about 2 moles/l, and the absolute amount of the fuel in the fuel circulation system is small.

Thus, in the present invention a fuel concentration sensor is used to detect the fuel concentration in the fuel circulation system to supply the fuel, or an output voltage or output current of the fuel cell is detected because the output voltage or current is reduced as the fuel concentration is lowered. When the detected value becomes lower than the standard concentration, a signal to open the valve to the fuel tank is emitted to supply the fuel to the fuel circulation system.

A considerably large amount of water is present in the fuel circulation system, and thus it is preferable to supply the water to the fuel circulation system to checking whether a predetermined amount of water is retained in the fuel circulation system satisfactorily or not. To this end, a liquid level sensor is provided in the fuel circulation system of the fuel cell to detect whether the liquid level becomes lower than the standard level or not.

- 1 When the liquid level is detected lower than the standard level, a signal to open the valve to the water tank is emitted to supply the water to the fuel circulation system.

In the present invention, two tanks, i.e. fuel  
5 tank and water tank, are provided, and only fuel is stored in the fuel tank and only water in the water tank. However, it is more preferable and more advantageous for the operation of the fuel cell to distribute the necessary amounts of fuel and water to the individual tanks, that is,  
10 to store mixtures of fuel and water in the individual tanks. When only fuel is supplied to the fuel circulation system from the fuel tank, higher fuel concentration is locally and transiently developed in the fuel circulation system owing to the restricted circulation rate, unpreferably  
15 lowering the fuel utilization efficiency transiently. This problem can be solved by storing a fuel-rich mixture of fuel and water in the fuel tank. Preferable molar ratio of water to fuel in the fuel-rich mixture is 5 - 0 : 1, where zero means only fuel. It is preferable to select a  
20 ratio approximating to the ratio of consumption rate of water to that of fuel on average during the operation of the fuel cell.

When only water is supplied to the fuel circulation system from the water tank, lower fuel  
25 concentration is likewise locally and transiently developed in the fuel circulation system owing to the restricted circulation rate, and the fuel becomes short locally, unpreferably lowering the performance of the fuel cell.

### BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 9 is a schematic view showing an apparatus for detecting a fuel concentration according to one



1 embodiment of the present invention.

Figs. 10 and 11 are schematic views showing apparatuses for detecting a fuel concentration according to other embodiments of the present invention.

5 Fig. 12 is a characteristic diagram showing a relationship between the fuel concentration and the detected electric current.

#### PREFERRED EMBODIMENTS OF THE INVENTION

One embodiment of the present invention will be  
10 described, referring to Fig. 6, where a liquid fuel cell using methanol as fuel and sulfuric acid as an electrolyte is illustrated. Electrodes 2 (fuel electrode 2-1 and oxidizing agent electrode 2-2) are each made from a porous carbon plate as a substrate and a catalyst of platinum-  
15 based substance supported on carbon powders, the catalyst being deposited on the substrate. Through a fuel chamber 4, a liquid mixture of methanol and dilute sulfuric acid, which, of course, contains water, is circulated as an anolyte by a pump 9. A carbon dioxide gas is generated at  
20 the fuel electrode 2-1 as a product gas 811.

Air is supplied to an oxidizing agent chamber 5 as an oxidizing agent 7, and the exhaust gas 82 contains formed water at the same time.

A liquid level sensor 12 is provided on the liquid  
25 level corresponding to the liquid level threshold value near the upper end of the electrodes 2 in the fuel circulation system. When the liquid level is lowered, the sensor

1 12 works to emit a signal to open the valve 111 and  
supply the necessary amount of water from the water tank  
101 to the fuel circulation system.

A methanol concentration sensor 13 based on the  
5 electrochemical reaction is provided in the fuel circulation  
system and set to the methanol concentration of 1 mole/l.  
When the methanol concentration in the fuel circulation  
system becomes lower than the set value, the sensor 13 works  
to emit a signal to open the valve 112 and supply the  
10 necessary amount of the fuel from the fuel tank 102 to the  
fuel circulation system. The valves may be pumps.

In a liquid fuel cell with the structure of Fig. 6  
and with a power output of 12 V and 100 W, the circulation  
rate of the anolyte in the fuel circulation system is set  
15 to 700 cc/min., and about 30 cc of water is supplied to  
the fuel circulation system from the water tank 101 with  
one opening of the valve 111 by the signal from the liquid  
level sensor 12 when the liquid level is lowered in the fuel  
circulation system. About 10 cc of fuel is supplied to  
20 the fuel circulation tank from the fuel tank 102 with one  
opening of the valve 112 by the signal from the methanol  
concentration sensor 13 when the fuel concentration becomes  
lower than 1 mole/l.

The fuel concentration during the operation of  
25 liquid fuel cell is not necessarily 1 mole/l, and operation  
at a higher fuel concentration is possible, if the load  
current is relatively large, whereas the operation at a  
lower fuel concentration is also possible, if the load

1 current is relatively small.

To set a fuel concentration, the set electric current must be changed, because the electric current is a function of fuel concentration according to the constant voltage system when the electrochemical reaction is utilized.

As described above, a liquid fuel cell with two tanks, i.e. a fuel tank containing only fuel and a water tank containing only water, can be operated stably against fluctuations in load current, operating temperature or atmosphere.

Another embodiment of the present invention will be described below, referring to Fig. 7, where, when the liquid level is detected lower by the liquid level sensor in the same liquid fuel cell as in Fig. 6, a water-rich fuel mixture is supplied from the water tank 101 in place of only water. That is, since the fuel concentration in the fuel circulation system is 1 mole/l, the water-rich fuel mixture in the water tank 101 is made to have a methanol concentration of 1 mole/l. That is, the molar ratio of methanol to water is about 0.02.

In place of measuring the fuel concentration in the fuel circulation system, such a phenomenon that the output voltage is lowered as the fuel concentration is decreased can be also utilized. To this end, a detector 15 to check an output voltage level is provided as shown in Fig. 7, and when a decrease in the output voltage level is detected, the valve 112 to the fuel tank 102 is opened with

- 1 a signal from the detector 15 to supply the fuel to the  
fuel circulation system. In that case, a fuel-rich mixture  
of fuel and water is supplied from the fuel tank 102  
in place of fuel only to suppress local and transient  
5 increase in the fuel concentration in the fuel circulation  
system. Molar ratio of water to methanol in the fuel-rich  
mixture in the fuel tank 102 is 2. In this case, total  
volume of the water and the fuel in both tanks is the same  
as in the embodiment of Fig. 6.
- 10 In this embodiment, both tanks 101 and 102 contain  
fuel mixtures, and local and transient unbalance of fuel  
concentration in the fuel circulation system can be largely  
improved, and thus the circulation rate by pump 9 through  
the fuel circulation system can be much reduced, and a  
15 good fuel cell performance can be obtained even at the  
reduced circulation rate of 200 cc/min.

Further embodiment of the present invention will  
be shown in Fig. 8, where only differences from the embodi-  
ment of Fig. 7 are that a signal for supplying a fuel-rich  
20 mixture from the fuel tank 102 to the fuel circulation  
system is emitted in accordance with a decrease in the load  
current of a liquid fuel cell. A detector 16 is connected to  
two end points of a resistor 18 at the fuel electrode 2-1  
and the valve is opened with a signal from the detector 16,  
25 and further that a portion or all of water contained in the  
exhaust gas 82 from the oxidizing agent chamber 5 is  
recovered in a trap 17 and returned to the tank 101. By  
the provision of the water recovery trap, the capacity of

1 water tank 101 can be reduced.

In the foregoing embodiments, liquid fuel cells using methanol as fuel and an acidic electrolyte have been described, but the present invention is readily applicable  
5 also to an alkaline type liquid fuel cell using methanol as fuel, and other liquid fuel cells using hydrazine, formaldehyde, etc. as fuel by providing the fuel cell with two tanks and selecting fuel-water ratios of fuel mixtures in the tanks, as described above.

10 When a apparatus for detecting a fuel concentration according to the following embodiments is used in the present liquid fuel cell, the effects of the present liquid fuel can be further improved as described below.

In Fig. 9, an apparatus 516 for detecting a fuel  
15 concentration according to one embodiment of the present invention is schematically given, which comprises an anode 517, a cathode 518, a power source 519 and a detector 520, as in the prior art, but the anode 517 has a fuel-controlling layer 517b' through a catalyst layer 521 in the  
20 present invention. The fuel-controlling layer 517b' is prepared from a carbon fiber paper treated with a suspension of fine polytetrafluoroethylene particles by baking to give a controlled permeation and a strong water repellency to the paper. The fuel permeation can be  
25 adjusted to, for example, about  $7 \times 10^{-6}$  moles/cm<sup>2</sup>.min.mole/l by the treatment. A platinum-based catalyst layer 521 is provided on one side of the layer 517b' by kneading the catalyst with the same suspension of fine polytetra-

10 side.

15 the other sides from direct contact with the anolyte.

20 mole/cm<sup>2</sup>.min.mole/l) and a fuel concentration is 0 to 1.5

The fuel-controlling layer 517b' for use in the

1 present invention is not only a fibrous carbon paper but  
can be also a porous carbon sheet, or can be an electro-  
conductive porous material such as sintered metal. In that  
case, the fuel-controlling layer must have only a function  
5 to control the permeation of fuel, and thus an insulating  
sintered ceramics or organic porous materials can be also  
used. To provide the catalyst layer on the fuel-controlling  
layer, various other techniques such as coating, deposition,  
electrophoresis, CVD, etc. can be also used.

10 In Fig. 10, another embodiment of the present  
invention is shown, where the fuel-controlling layer is  
used double. That is, a second fuel-controlling layer 517c  
is provided on the fuel-controlling layer 517b' at the  
cathode-facing side, where the second fuel-controlling  
15 layer 517c is prepared from a kneaded mixture of carbon  
powders or graphite fluoride powders with a suspension of  
fine polytetrafluoroethylene particles having a water  
repellency and an adhesiveness by applying the kneaded  
mixture to the surface of fuel-controlling layer 517b',  
20 followed by baking to integrate these two layers. Cathode  
518 is prepared from a cathode plate 518a other than a  
platinum plate and a catalyst layer 518b laid on the cathode  
plate by deposition or by electrophoresis, and no special  
material is required for the cathode plate 518a. That is,  
25 a cathode with a good detection sensitivity can be obtained  
at a low cost.

In Fig. 11, other embodiment of the present  
invention is shown, where the cathode is improved by

15 Further, according to the present invention, an anode electrode having a fuel-controlling layer deposited thereon through a catalyst layer is used in the present apparatus for detecting a fuel concentration, and thus no liquid fuel stagnation occurs between the anode electrode  
20 and the fuel-controlling layer, improving the permeation of liquid fuel and activation of the reaction between the electrodes as well as improving the detection sensitivity and response and thus the reliability of the apparatus.



WHAT IS CLAIMED IS:

1. A liquid fuel cell having a circulation system for a fuel mixture comprising fuel and water, which comprises a first tank (101) containing water or a water-rich fuel mixture comprising water and fuel, a second tank (102) containing fuel or a fuel-rich mixture comprising water and fuel, a first detector (12) for detecting the liquid level of the fuel mixture in the circulation system, a second detector (13) for detecting a fuel concentration of the fuel mixture in the circulation system, or an output from the fuel cell, or a load current of the fuel cell, a valve means (111) for controlling flow of the water or the water-rich mixture in the first tank to the circulation system in accordance with the output from the first detector (12), and a valve means (112) for controlling flow of the fuel or the fuel-rich mixture in the second tank to the circulation system in accordance with the output from the second detector (13).
2. A liquid fuel cell according to claim 2, wherein the water-rich mixture in the first tank (101) is a mixture of water and fuel having a molar ratio of fuel to water of not more than 1, and the fuel-rich mixture in the second tank (102) is a mixture of water and fuel having a molar ratio of water to fuel of not more than 5.
3. A liquid fuel cell according to claim 1 or 2, wherein the fuel is methanol.

4. A liquid fuel cell according to claim 1, wherein means (17) for recovering water discharged from an oxidizing agent chamber of the fuel cell into the first tank are provided.

5. A liquid fuel cell having a circulation system for a fuel mixture comprising fuel and water, which comprises a first tank (101) containing water or a water-rich fuel mixture comprising water and fuel, a second tank (102) containing fuel or a fuel-rich mixture comprising water and fuel, a first detector (12) for detecting the liquid level of the fuel mixture in the circulation system, a second detector (13) for detecting a fuel concentration of the fuel mixture in the circulation system, a valve means (111) for controlling flow of the water or the water-rich mixture in the first tank (101) to the circulation system in accordance with the output from the first detector (12), and a valve means (112) for controlling flow of the fuel or the fuel-rich mixture in the second tank (102) to the circulation system in accordance with the output from the second detector (13), the second detector (13) being an apparatus for detecting a fuel concentration by electro-chemical reaction and comprising an anode electrode (517) provided with a fuel-controlling layer (517b') for controlling permeation of fuel through a catalyst layer (521), a cathode electrode (518), a power source (519) and a detector (520), the anode electrode (517) and the cathode electrode (518)

being dipped in the fuel mixture and a voltage being applied to the electrode.

6. A liquid fuel cell according to claim 5, wherein the fuel is methanol.

7. A liquid fuel cell according to claim 5 or 6, wherein the water-rich mixture in the first tank (101) is a mixture of water and fuel having a molar ratio of fuel to water of not more than 1, and the fuel-rich mixture in the second tank (102) is a mixture of water and fuel having a molar ratio of water to fuel of not more than 5.

8. A liquid fuel cell according to claim 5, wherein means (17) for recovering water discharged from an oxidizing agent chamber of the fuel cell into the first tank are provided.

9. A liquid fuel cell according to claim 5, wherein the anode electrode has a second fuel-controlling layer (517c) on the fuel-controlling layer (517b').

10. A liquid fuel cell according to claim 5, wherein the cathode electrode comprises a cathode plate (518a) other than a platinum plate, and a catalyst layer (518b).

11. A liquid fuel cell according to claim 5, wherein the cathode electrode comprises a cathode plate (518a) other than a platinum plate, an electroconductive porous layer (518c) and a catalyst layer (518b).

FIG. 1 PRIOR ART

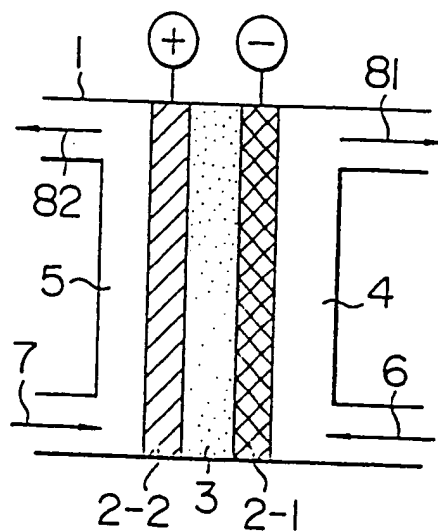


FIG. 2 PRIOR ART

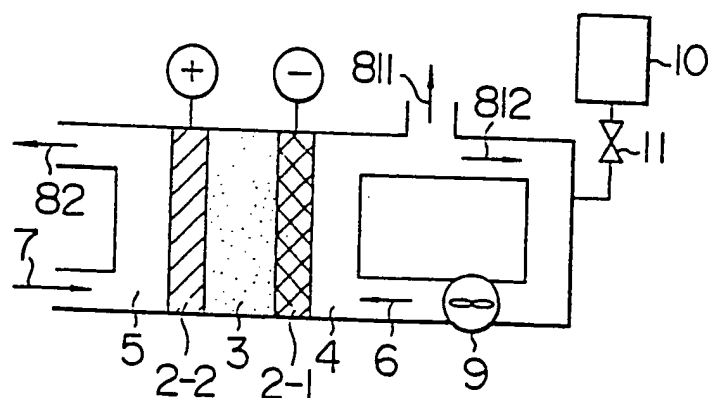


FIG. 3

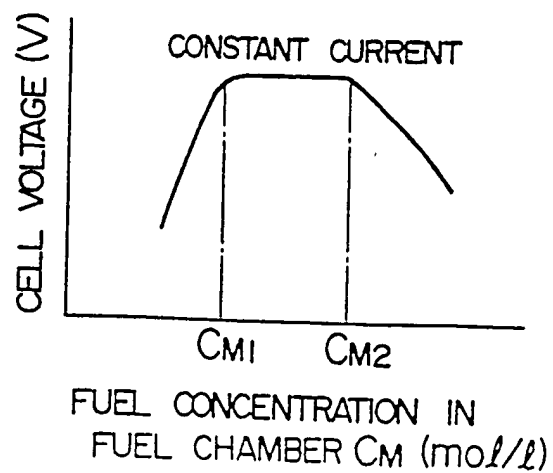


FIG. 4 PRIOR ART

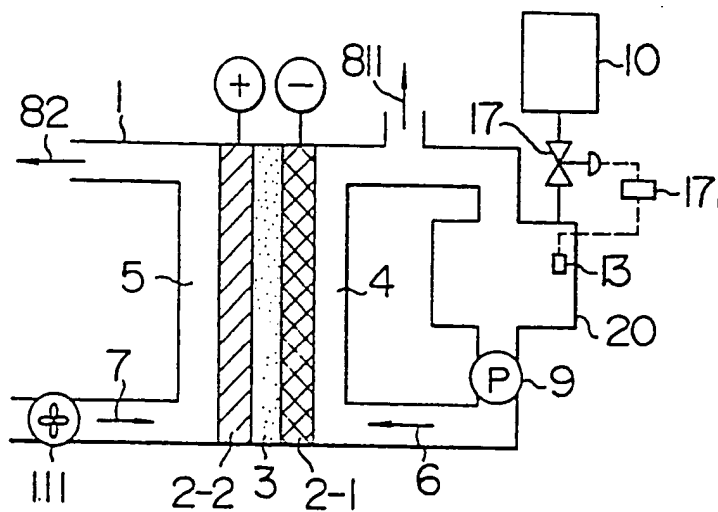
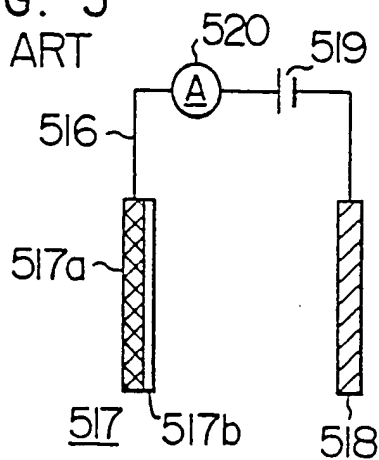
FIG. 5  
PRIOR ART

FIG. 6

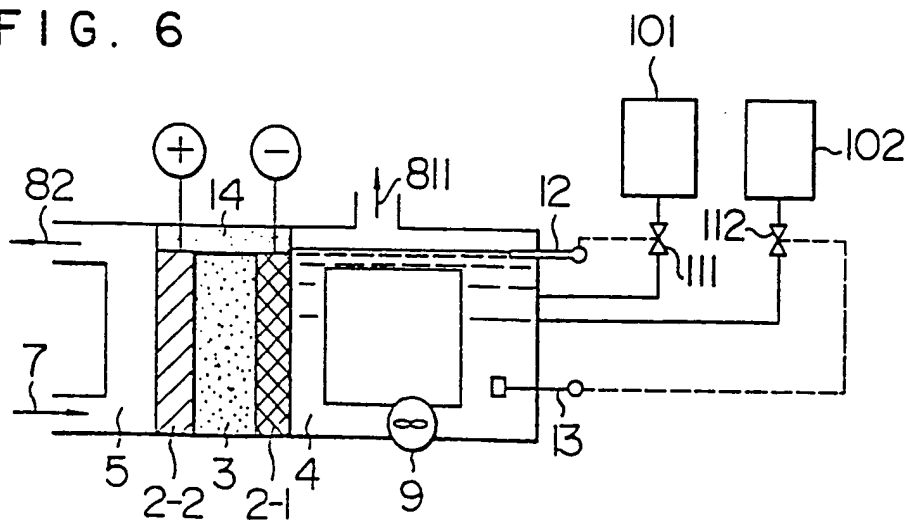




FIG. 9

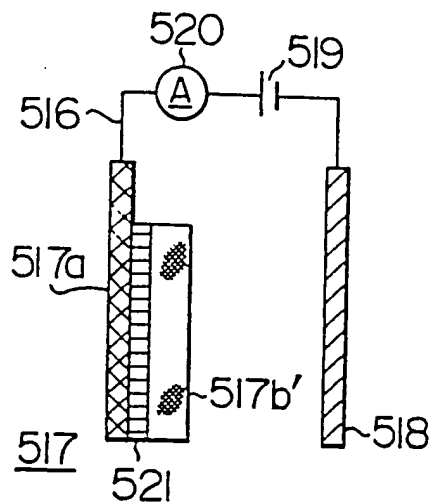


FIG. 10

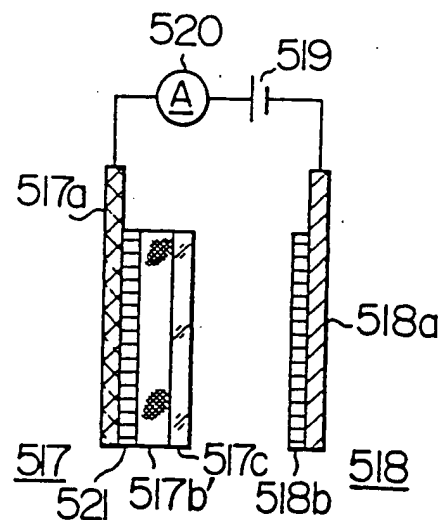


FIG. 12

